RAI 318

Water Recovery Study

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ABSTRACT

Ultrafiltration studies conducted on synthetic and real urine during the report period have led to the selection of cellulose acetate as the most promising membrane material.

Using specially cast cellulose acetate membranes and real urine it has been possible to produce water which meets the United States Public Health Service specifications for chloride, ammonia and total solids in drinking water at fluxes (rate of product water formation) of 9-13 liters per foot square of filtration surface per operation day.

1.0 DISCUSSION OF RESULTS

1.1 Apparatus

The experimental ultrafiltration apparatus and procedures are detailed in the Experimental Section (2.0). Our ultrafiltration apparatus and procedures are quite versatile and allow us to study the effect of varying such experimental parameters as

a. Feed solution

b. Membrane properties

c. Pressure

d. Temperature

e. Linear flow rate of feed.

Not all of these parameters have been varied in our work to-date. Thus, based on the reported results of Loeb and coworkers on the ultrafiltration of sea water,[1,2] we are confining, for the time being, our studies to the 1500-2000 psi range. Actually, our work to-date has been performed only at 2000 psi. Furthermore, since Loeb[1,2] has found that high linear flow rates of feed solution are desirable, our work has been done with the highest flow rate possible with our experimental system. Since temperature affects both water flux and solute rejection, it was deemed necessary to work under constant temperature conditions. The bulk of the work reported in this communication was performed at 32-45°C. Our experimental apparatus has been modified so as to allow control of temperature to ±0.5°C. All future experiments will be performed at 30°C.±0.5°C. unless temperature is the parameter to be studied.

1.2 Ultrafiltration of Urine

An evaluation of commercially available films in the RAI experimental ultrafiltration system failed to yield any materials with promising activity. In view of this finding the program was directed toward the synthesis of membranes with suitable activity. The most suitable membranes prepared to date are those which are prepared from cellulose acetate via a special casting technique.

Two separate approaches to the problem of recovering potable water from urine via ultrafiltration were investigated during this report period. One involved the ultrafiltering of urine solutions without any prior pre-treatment. In studying this approach synthetic urine solutions were investigated which contained sodium chloride and urea. The second approach studied involved the pre-treatment of urine with urease to convert the urea to ammonia and carbon dioxide. This was followed by acidification with citric acid in order to convert the ammonium carbonate to ammonium citrate. (The urease treated urea consists of ammonia and carbon dioxide which form ammonium carbonate to some extent but the concentration of free ammonia is very high in such solutions. For this reason the ammonia, carbon dioxide plus ammonium carbonate solution was acidified with citric ion acid to completely convert the ammonia to ammonium ion. The ultrafiltration of a synthetic urine solution of ammonium carbonate (Experiment No. 156-72B) showed only 82% ammonia rejection.)

The difference between the two approaches is simply that the first one is attempting to ultrafilter the nitrogen in the form of the non-ionic urea molecule while in the latter, one is ultrafiltering the ionic ammonium species. The results of our studies with synthetic urine solutions are shown in Table I_A. The experiments involving the urea ultrafiltration are shown as Experiments Nos. 156-73A through 76C; those involving the use of ammonium ion are shown in Experiment Nos. 156-62B through 72B. As is readily evident from these results the ammonium species are much more easily rejected than the urea molecule.

It is seen from the results in Table I_A that the pre-treatment procedure actually gives effluents which can be classified as potable water by U.S. Public Health Service specifications. Because of this highly encouraging result it was decided to investigate this technique with actual urine as a feed solution. Urine was collected, treated with urease, acidified with citric acid and then charged into our ultra-filtration apparatus. The results of these experiments are seen in Table I_B. The results with urine follow very closely those for the synthetic urine solutions. Analyses of the effluents showed that they passed the U.S.P.H.S. specifications for chloride, ammonia, and total solids. This approach to the problem of water recovery from urine is being followed up in greater detail to optimize the various experimental and engineering parameters.

The fact that success has been achieved with the pre-treatment technique has not at all meant the cessation of attempts to improve the direct ultrafiltration of urine without pre-treatment. Such a direct ultrafiltration is highly desirable from all points of view as regards weight, volume, A B

TABLE I_A - Ultrafiltration of Synthetic Urines

Exp. No. 156-	Membrane Thickness mils	Membrane Quench Time, min.	Membrane Anneal. Temp. °C.	Cell Press. psi	Effluent Flux, l./ft.^{2}/day	Cl^- in parts per million Feed	Cl^- in parts per million Effluent	% Cl^- Rejection (A)	Total NH_3 parts per million Feed	Total NH_3 parts per million Effluent	% Total NH_3 Rejection (A)	Total Solids in parts per million (B)	Solution under Investigation
62B	20 (E)	2	78	2125	9.39	3298	118	96	12820	93	99.3	-	NaCl, Diammonium citrate
62C	20 (E)	4	78	2100	6.68	3298	94	97	12820	92	99.3	-	"
63B	20 (E)	2	80	2125	11.79	3581	219	94	9500	511	95	-	"
65B	20 (E)	1	82	2050	11.80	4000	197	95	14000	231	98	-	"
66A	20 (E)	2	82	2125	12.01	4000	133	97	14340	101	99.3	-	"
66B	20 (E)	2	82	2075	11.60	4000	110	97	14340	93	99.4	-	"
67B	20 (E)	2	82	2100	13.81	3786	140	96	13200	82	99.4	-	"
67C	20 (E)	4	82	2100	9.26	3786	119	97	13200	89	99.3	-	"
69B	20 (E)	2	80	2050	17.55	4010	173	96	13800	122	99.1	-	"
69C	20 (E)	4	80	2050	10.49	4010	267	93	13800	166	99	-	"
71B	20 (E)	2	82	2150	11.82	3914	135	97	14000	142	99	-	"
72B	20 (E)	2	82	2125	11.13	4000	192	95	10512	1890	82	-	NaCl, Diammonium carbonate
73A	20 (E)	1/2	78	2200	29.69	4380	172	96	13432	4176	69	-	NaCl, urea
74A	10 (D)	4	82	2150	1.96	4177	253	94	13110	3491	73	-	" "
75C	10 (D)	4	82	2000	2.56	3305	177	95	12680	2027	84	-	" "
76A	10 (D)	4	82	2000	3.38	3219	109	97	12222	3219	74	-	" "
76B	10 (D)	4	82	2000	1.91	3219	157	95	12222	3018	75	-	" "
76C	10 (D)	4	82	2000	1.83	3219	160	95	12222	2608	78	-	" "

A B

TABLE I_B - Ultrafiltration of Urine

Exp. No. 156-	Membrane Thickness mils		Membrane Quench Time, min.	Membrane Anneal. Temp. °C.	Cell Press. psi	Effluent Flux, l/ft.^{2}/day	Cl^- in parts per million Feed	Cl^- in parts per million Effluent	% Cl^- rejection (A)	Total NH_3 parts per million Feed	Total NH_3 parts per million Effluent	% Total NH_3 Rejection (A)	Total Solids in parts per million(B)	Solution under Investigation
78A	20	(E)	1/2	82	2000	9.44	6269	153	97	12292	102	99.2	340	Urine (C)
78C	20	(E)	2	82	2000	9.44	6269	160	97	12292	91	99.3	366	Urine (C)
84A1	20	(E)	1	83	2000	13.53	5379	123	98	8654	64	99.2	390	Urine (C) (F)

FOOTNOTES TO TABLES I_A AND I_B

(A) $$\%\ \text{Rejection} = 100 - \frac{\text{concentration of species in effluent}}{\text{concentration of species in feed}} \times 100$$

(B) The United States Public Health Service specifies that 500 parts per million is the maximum allowable concentration of dissolved solids in a drinking water supply.

(C) The urine employed was collected amongst the male members of the RAI staff. It was allowed to sediment for 1-1/2-3 days in the presence of 1 gm./liter of urease. At the end of this period it was decanted, acidified with citric acid, and charged into the reservoir of the ultrafiltration apparatus.

(D) Casting solution temperature -20 $\longrightarrow$ -25°C., glass plate temperature 3°C., quench interval temperature 3°C.

(E) Casting solution temperature -20 $\longrightarrow$ -25°C., glass plate temperature -17°C., cast and drawn down at RT, placed in refrigerator at -17°C. and quench interval measured in refrigerator at -17°C.

(F) Feed solution temperature (reservoir) controlled at 30 ± 0.5°C. All others run at temperatures from 32-45°C.

efficiency, etc. In studying Experiment No. 156-75C of Table I_A it is evident that a slight improvement over the results of this experiment would make possible the use of a two-pass direct ultrafiltration system. Thus, if the ammonia rejection could be increased from 84% to 91%, one could readily visualize a two-pass system which would result in 99+% rejection of urea and thus yield a potable water on a direct ultra-filtration method with no pre-treatment. Work in this direction as regards membrane fabrication is in progress.

1.3 Membrane Fabrication

As indicated above in Section 1.2, the membranes which have been found useful in this study are specially cast cellulose acetate membranes. The activity of these membranes has been found to be quite good and it has been possible to greatly vary the properties of these membranes. Thus, by varying such parameters as casting solution composition, casting solution temperature, temperature of casting, temperature during quenching, length of quench period and temperature of the annealing process, one is able to prepare a variety of membranes with different water fluxes and solute rejection properties. Due to the extreme cold temperatures employed in the casting procedure, a high degree of lack of reproducibility in membranes has been observed. A large segment of the work for the coming quarterly period will involve further investigation of the experimental parameters necessary for obtaining reproducible membranes. As mentioned in Section 1.2 above the bulk of our experimental membrane program will be aimed towards fabricating membranes which will reject urea in high enough rejection to allow a direct (non-pretreatment) ultrafiltration of urine.

2.0 EXPERIMENTAL PROCEDURES AND APPARATUS

2.1 Experimental Ultrafiltration System

The experimental ultrafiltration system is depicted in Figure I. This apparatus is a laboratory unit and bears no resemblance to a prototype unit. All parts of the system are made of 316 stainless steel to prevent corrosion. In operation the urine reservoir (A) is charged with the urine feed which is then passed at atmospheric pressure into the line cartridge filter (B) to filter out particulate matter and into the diaphragm pump (C). The diaphragm pump (Milton Roy Co.) discharges the feed at any desired pressure (to 2500 psi) and flow rate (to approximately 600 ml. per minute). The urine feed, which is now under pressure, is then forced through coils in the bath (D) in order to maintain the system temperature constant to within 0.5°C. and from there into the ultrafiltration cell (E) where it flows across the (porous plate-filter paper supported) membrane. The ultrafiltration cell itself is shown disassembled and assembled in Figures II and III, respectively. The product water leaves the bottom of the ultrafiltration cell (after traversing the membrane, filter paper, and porous plate in that order) and is collected in the receiver (J). The feed solution after leaving the cell (E) goes through the gas activated (I) back pressure valve (G) where the pressure returns to atmospheric and on through the flow meter (H) on its way back to the urine reservoir (A) for recycling.

This experimental setup allows one to easily vary such operations parameters as pressure, temperature, and linear flow rate over the membrane surface. In most of our experiments to date, the pressure has been maintained at 2000 psi.

FIGURE I — EXPERIMENTAL ULTRAFILTRATION SYSTEM

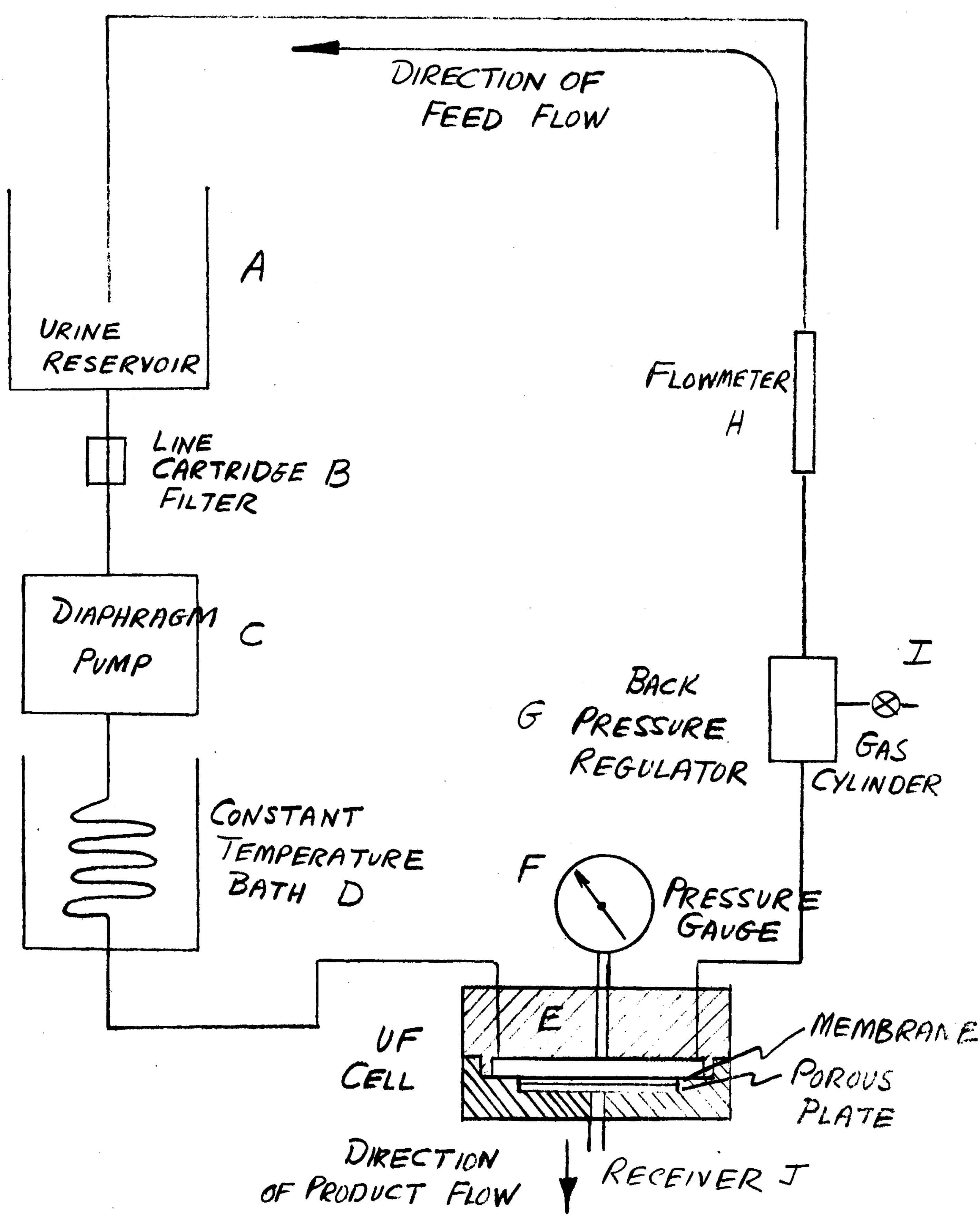
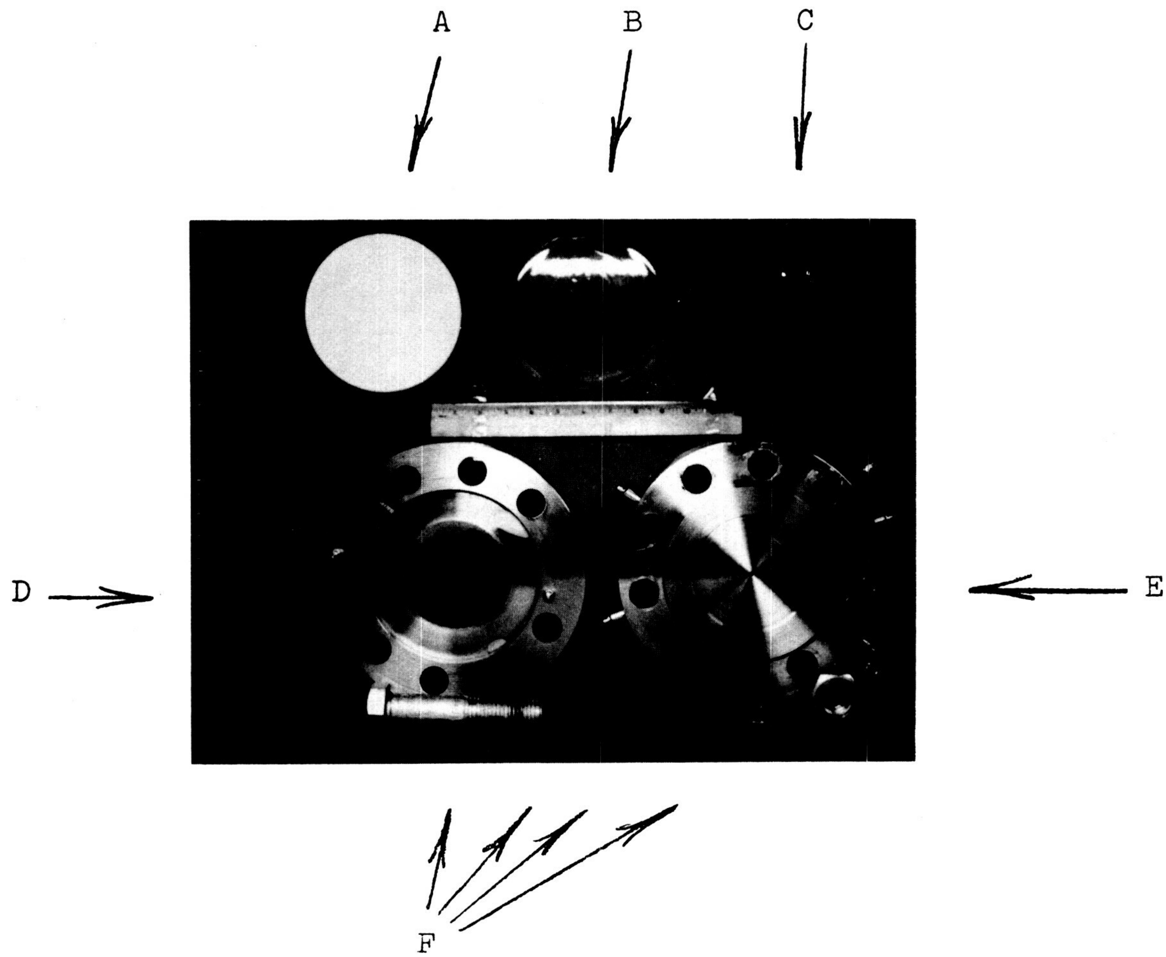


FIGURE II - Experimental Ultrafiltration Cell (Disassembled)



A - Filter Paper Membrane Underlay

B - Membrane

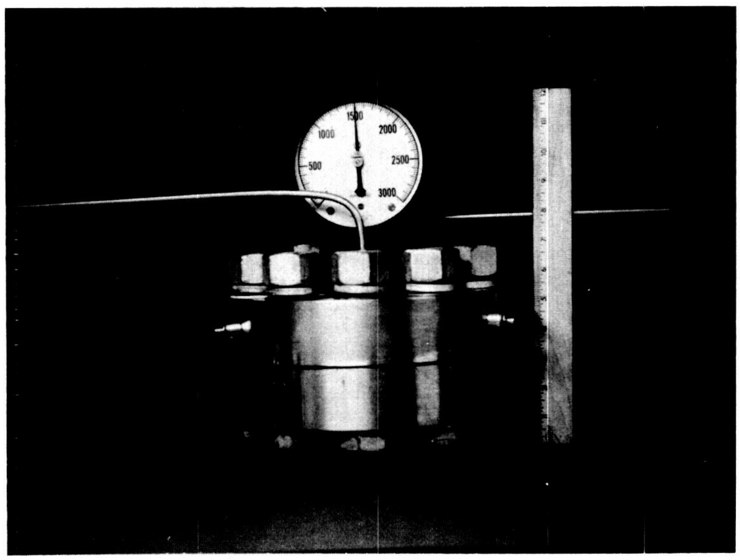
C - Neoprene Gasket

D - Lower half of cell showing 3.73" diameter press fit stainless steel porous plate, sealing surface, and alignment pins.

E - Upper half of cell showing inlet and exit ports.

F - (10)-1" diameter nuts, bolts, washers, and lock washers.

FIGURE III - Experimental Ultrafiltration Cell (Assembled)



Cell is shown bolted together. The feed and exit lines are also shown.

Most of the experiments to date were performed before the temperature controlling unit was installed and were performed under ambient conditions which resulted in a system temperature of 32-45°C. Since the installation of the temperature controlling unit, all experiments are being performed at 30±0.5°C. (The temperature of the bath is controlled by a thermoregulator immersed in the feed reservoir. Thus, the bath temperature is maintained at whatever temperature is required in order to keep the feed at 30°C.)

The cavity in the ultrafiltration cells is a 4 inch cylinder with a height of 1/16 inch. In operation, the top part of the cell is raised from the bottom part by the sealing gasket. This results in a final cylindrical 4 inch diameter cavity over the membrane surface of ca. 3/32 inch height. The linear flow rate over the membrane surface employed in all of our experiments is ca. 5 cm./sec. as calculated for the straight line flow connecting the inlet and outlet parts and ca. 4 cm./sec. for the maximum (i.e., 4 inch diameter) cross-sectional area perpendicular to the direction of flow.

2.2 Preparation of Membranes

a. Casting Solution

The casting solution composition used in the preparation of the membranes in Tables I_A and I_B has the following composition:

Cellulose Acetate (E 398-3) Eastman Kodak Co.	= 44.4 grams
Acetone	= 133.4 "
Magnesium Perchlorate	= 2.2 "
Water	= 20.0 "
Total	= 200.0 grams

The ingredients were weighed into wide-mouthed, teflon gasketed bottles, closed, placed on a roll mill until solution is complete and then cooled to an appropriate temperature.

b. Casting Procedure

The cold casting solution is poured onto a cold glass plate and a doctor blade drawn across the plate. This leaves a wet film of uniform thickness on the glass plate. The plate containing the film is then placed in a cold environment for a time interval (the quench period) and then quickly immersed in an ice-water bath for 1 hour. The temperatures of the casting solution, glass plate, and cold environment during the quench interval and the length of the quench period are all important parameters in determining the properties of the membrane.

c. Annealing Cycle

After the immersion in ice-water, the film was peeled from the glass plate and placed in a circulating water bath and heated from room temperature to the annealing temperature and held at this temperature for 20 minutes. The bath was then allowed to cool to room temperature. The film was then considered ready for use. It is important that the side of the membrane facing the glass plate during the casting operation face the porous plate during the ultrafiltration operation.

The annealing temperature is very important as regards the final membrane properties. Our work has involved a study of annealing temperatures from 75 to 90°C.

2.3 Analytical

1. Bacteriological Quality

The bacteriological quality of two effluents from a real urine experiment is currently being investigated by an independent outside laboratory. The total bacteria and coliform group organisms are being measured. The results of these measurements will be reported at a later date.

2. Chloride Ion - The Volhard Method

In this method the chloride ion containing sample is titrated with an excess of standard silver nitrate as per the equation below:

$$Ag^+ + Cl^- \longrightarrow AgCl\downarrow + Ag^+$$

The excess silver ion is then back-titrated with standard thiocyanate solution

$$Ag^+ + SCN^- \longrightarrow AgSCN$$

the first drop of excess thiocyanate reacts with ferric alum indicator to give the colored Ferrithiocyanate ion

$$6SCN^- + Fe^{+++} \longrightarrow \underset{\text{soluble red-orange-brown}}{Fe(SCN)_6^{\equiv}}$$

Nitrobenzene is added at the end of the silver nitrate titration to prevent the equilibration of thiocyanate ion with precipitated silver chloride via the following reaction which would yield high results

$$AgCl + CNS^- \longrightarrow AgCNS + Cl^-$$

3. Total Ammonia - The Indophenol Method

The analysis of total ammonia is the sum total of ammonia, ammonium ion, and ammonia available from urea (2 moles per mole) contained in a given sample.

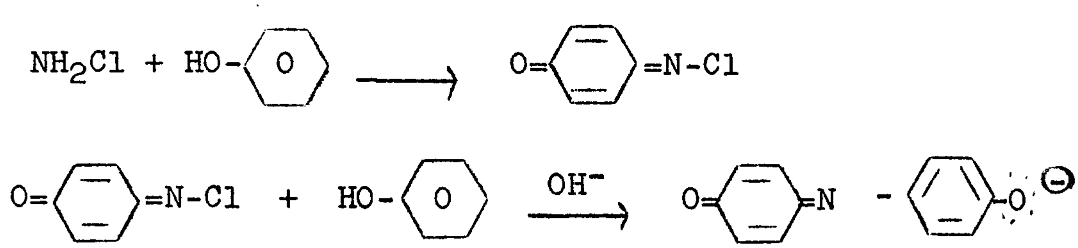
The analytical method is essentially a two-step reaction in which the urea is first converted to ammonia and carbon dioxide under the influence of the enzyme urease

$$H_2N\text{-}\underset{\underset{O}{\|}}{C}\text{-}NH_2 + 3H_2O \xrightarrow{\text{urease}} 2NH_4OH + CO_2$$

The liberated ammonia (or ammonium hydroxide) is then reacted with hypochlorite to yield chloramine

$$NH_3 + OCl^- \longrightarrow NH_2Cl + OH^-$$

which is then believed to react stepwise with phenol to yield finally the intense blue indophenoxide anion which is measured photometrically. The sequence is depicted in the following equations



Blue, absorption max. near 6250 Å

4. Total Dissolved Solids

The U.S. Public Health Service states that 500 parts per million ($\sim$500 mgs. per liter) is the maximum solids allowable in a given drinking water supply. Our procedure for the determination of solids entails the drying of a sample of unit volume to constant weight at 50°C. and weighing the non-volatile residue.

3.0 REFERENCES

1. S. Loeb, and G.R. Nagaraj, Paper presented at American Chemical Society Meeting, Los Angeles, Calif., April 4, 1963.

2. S. Loeb and F. Milstein, Dechema Monographien 47, Part II (1962).